

MOBILITY, TOXICITY AND VOLUME OF COAL TAR AT A FORMER MANUFACTURED GAS PLANT SITE

A.T. Zimmerman¹, P.E.

AUTHOR: ¹Senior Licensed Engineer, Zimmerman Technical Services, Inc., 3595 Canton Road, Suite A-9271, Marietta, Georgia 30066
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Abstract. Prior to the widespread construction of interstate natural gas pipelines in the 1950s, gas manufactured from coal, petroleum or other hydrocarbon feedstock was produced for lighting and heating purposes by local utilities in cities and towns across the United States. By-products and wastes generated at these plants were commonly disposed of on site.

Major wastes and by-products included tar and oil residues, spent oxides and ash materials. These materials can be a continuing source of pollutants threatening both groundwater and surface water bodies. Pollutants include a complex mixture of hundreds of volatile organic compounds (VOCs), polynuclear aromatic hydrocarbons (PAHs), heavy metals and cyanides.

A former manufactured gas plant (MGP) is located in downtown Clayville, Georgia, on the south bank of the Indian River. Facility and geographic names have been changed to protect the privacy of the parties involved.

By-products from the plant were estimated at 14,000 tons of coke and 22,000 gallons of tar in 1929. Disposal practices at smaller MGP sites typical of the subject facility included landfilling of purifier (oxide) wastes, tar sludge, ammonia recovery wastes, ashes, clinkers, coke wastes, building material wastes, etc.

Based upon available data from the public record, and the history of this and other former MGP sites, the mobility, toxicity, and volume of free-phase coal tar in the subsurface has been estimated along with its associated environmental contamination. Results indicated that up to 300,000 gallons of free-phase liquid coal tar may remain in the subsurface soils and aquifer.

The residual tar and other MGP contaminants have resulted in groundwater contamination exceeding the Georgia drinking water standards. Groundwater under the site is hydraulically connected with the adjacent major river with possible movement of contaminants into the local ecology.

INTRODUCTION

From as early as 1816 and into the 1960s, manufactured gas for lighting and heating in the United States was produced by local utilities from coal, oil, or a combination of both. Prior to the 1940s, there were more than 1,000 such plants throughout the United States. By the 1950s, most plants had ceased operation due to the construction of interstate pipelines delivering natural gas; a less-expensive product with a higher heating value (Chapman, et al, 1990).

Gas plant by-products and wastes were commonly disposed of on site, particularly at smaller facilities. Larger facilities might find

it economical to market some of their residuals, but nonetheless would dispose of them on site if the market price was not sufficient to warrant the effort of collection for sale.

Major wastes and by-products included tar and oil residues, spent oxides and ash materials. These materials can be a continuing source of pollutants threatening both groundwater and surface water bodies. Pollutants include a complex mixture of hundreds of volatile organic compounds (VOCs), polynuclear aromatic hydrocarbons (PAHs), heavy metals and cyanides (USEPA, 1988).

A Case Study

The subject facility was formerly a manufactured gas plant (MGP) located in downtown Clayville, Georgia, on the south bank of the Indian River. Facility and geographic names have been changed to protect the privacy of the parties involved.

Records are publicly available at the Georgia Environmental Protection Division (GEPD) documenting the site history and activities. These include results of a preliminary assessment and site investigation (PA/SI) completed in October 1991 and February 1992, respectively, and a remedial investigation and compliance status report (RI/CSR) completed in May 1996.

A three-story brick building and parking lot occupy the site. The ground floor is used by commercial establishments with residential condominiums above.

The site history can be traced back to January 1860, when construction of the first gas works was completed. Various changes were made to the facility throughout the following decades.

Four gas holders were eventually constructed with capacities ranging from 6,000 to more than 12,000 cubic feet. Gas production peaked in 1929 at a total of 35 million cubic feet. Figure 1 shows the site layout and estimated extent of free-phase coal tar in the subsurface.

According to records at the GEPD, the production of by-products was estimated at 14,000 tons of coke and 22,000 gallons of tar for the year 1929. According to USEPA (1988), disposal practices at facilities typical of the subject site included landfilling of purifier (oxide) wastes, tar sludge, ammonia recovery wastes, ashes, clinkers, coke wastes, building material wastes, etc. These were disposed of in whatever ditch, depression, pit or pothole was convenient.

In 1985, during the course of construction in connection with the renovation and development of the property, a construction equipment rig broke through the surface of the ground and exposed an underground pit containing coal tar waste. This was likely the remains of the 6K-ft³ gas holder foundation.

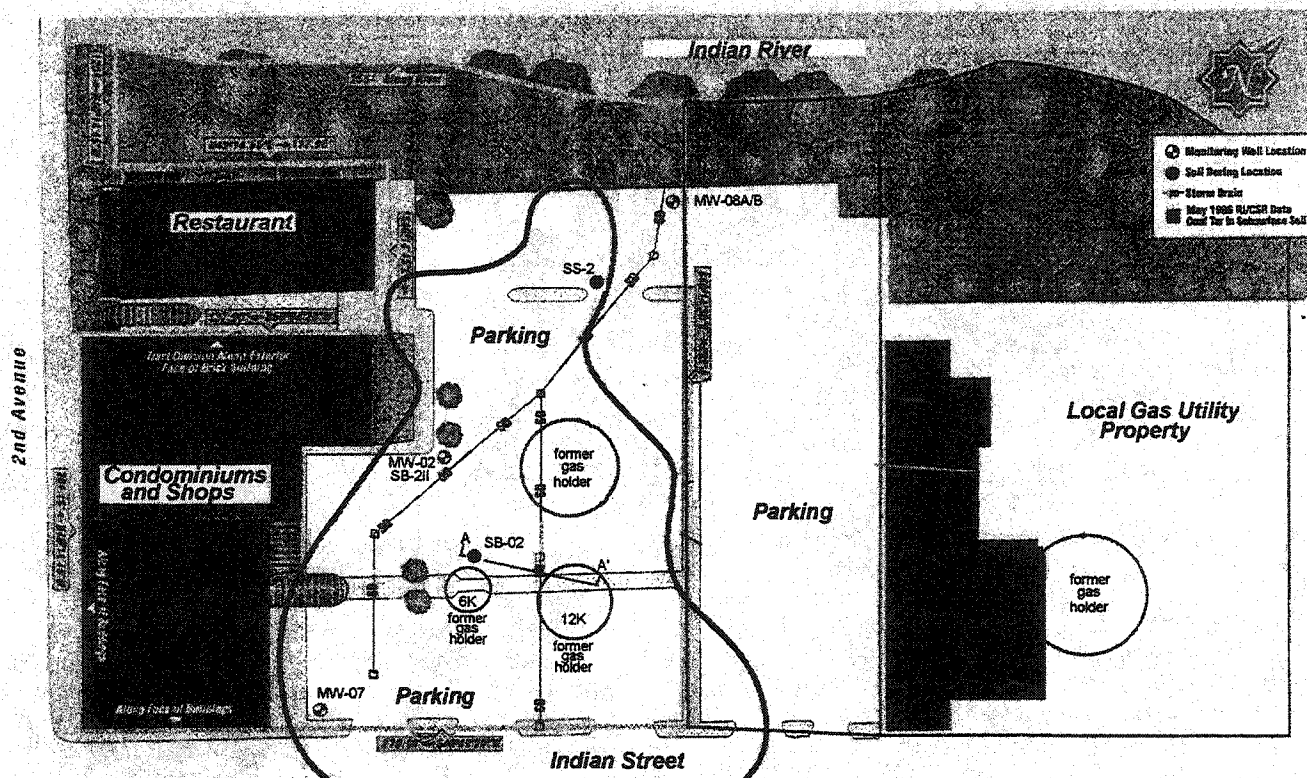


Figure 1. Site layout and estimated area of coal tar affected soils in the subsurface.

A sample was collected from the waste and submitted to an off-site laboratory for analysis. Results indicated the waste was forty per cent naphthalene with the remainder divided among other VOCs and PAHs.

Based upon results of the laboratory analysis, GEPD classified the tar as a listed hazardous waste under the Resource Conservation and Recovery Act (RCRA). The waste was described as similar to "decanter tank tar sludge from coking operations" (RCRA waste number K087). This waste is listed for the constituents of phenol and naphthalene. The USEPA directed a removal action under CERCLA and determined that the local gas utility was a potentially responsible party (PRP).

The gas utility completed a preliminary assessment and site investigation (PA/SI) in 1991 and 1992. The present landowner reported these results to the GEPD in May 1994 to comply with the state Hazardous Sites Response Act (HSRA). The GEPD responded by placing the site on the state Hazardous Sites Inventory (HSI) and directing submission of a remedial investigation and compliance status report (RI/CSR) in May 1996.

MOBILITY, TOXICITY AND VOLUME OF RELEASE

The organic materials of primary interest at MGP sites are the tar, oil and associated sludges that are complex mixtures of different PAHs and lesser amounts of phenolics and light aromatic VOCs. Cyanides and heavy metals can also be a significant concern.

However, for the purposes of this case study we considered only the issues related to the organics. Once discharged to surficial soils, the complex mixtures can slowly separate into different chemical classes (e.g. PAHs, phenolics, VOCs) that each behave

differently in soil and ground water.

Table 1 lists selected contaminants of concern along with some of their properties. The contaminants were selected based upon their relative mobility, toxicity and volume in the subsurface.

The site is built upon approximately 20 feet of fill with the greatest thickness near the river, gradually thinning to about 10 feet toward the street at the south boundary. Within the fill have been found buried building debris, coal, ash, clinkers, and coal tar by-product. The groundwater table normally occurs about 20 to 30 feet below the surface, but can vary significantly with changes in the river stage.

Below the fill are alluvial deposits of sand, silt and clay to a depth of about 30 feet. A semi-confining siltstone underlays the alluvium and is approximately 25 to 30 feet thick. A widely varying lens of silt, 5 to 30 feet thick, separates the siltstone from the limestone bedrock.

The majority of contamination appears confined to the surficial fill and alluvium, although PAHs were detected in the silt at 64.0 feet depth adjacent and to the north of the 6K-ft³ gas holder. Free-phase coal tar is indicated in several borelogs in that area and elsewhere around the site.

Figure 2 is an east-west cross section (A-A') through the center of the site near the former locations of the 6K and 12K-ft³ gas holders. A plan view of the cross-section location is shown on Figure 1.

Mobility of DNAPLs and Dissolved Species

Dense, non-aqueous phase liquids (DNAPLs) are defined as liquid substances relatively insoluble in water with a specific gravity greater than 1.0. Given a reported specific gravity for coal tar of 1.028 (at 45 °C), and the generally non-polar nature of its

Table 1. Contaminants of Concern, Their Properties and Estimate of Total NAPL Volume Per Cubic Meter of Affected Soils

		soil density=		2.65 g/cc		gas const.=		8.21E-05 atm-m3/mol-K		
		porosity=		0.55		temp =		293.15 K		
		org. carbon=		0.025						
COMPOUND CLASS	COMPOUND	MOLE FRACTION (decimal)	MAX GW CONC. (g/m3)	MAX SOIL CONC. (g/m3)	DENSITY (g/cc)	WATER SOL. (g/m3)	Kow (decimal)	HENRY'S LAW (atm-m3/mol)	TOTAL MASS (grams)	NAPL VOLUME (m3)
Volatiles	benzene	0.00051	0.8900	150	0.8737	1.75E+03	1.32E+02	5.59E-03	178.88	0.40
	toluene	0.00052	0.2800	450	0.8623	5.35E+02	5.37E+02	6.37E-03	536.63	1.18
	ethylbenzene	0.00211	0.3200	97	0.8670	1.52E+02	1.41E+03	6.43E-03	115.67	0.06
PAHs	xylene, total	0.00297	0.5200	910	0.8642	1.75E+02	8.91E+02	5.10E-03	1085.18	0.42
	acenaphthene	0.01111	0.0380	180	1.0242	3.42E+00	1.00E+04	9.20E-05	214.65	0.02
	benzo(a)pyrene	0.08333	0.0001	87	1.3510	1.20E-03	1.15E+06	1.55E-06	103.75	0.00
	chrysene	0.55556	0.0010	55	1.2740	1.80E-03	4.07E+05	1.05E-06	65.59	0.00
	naphthalene	0.00473	0.1500	800	1.1620	3.17E+01	2.76E+03	1.15E-03	954.00	0.17
	phenanthrene	0.00200	0.0020	390	1.1790	1.00E+00	2.88E+04	1.59E-04	465.08	0.20

constituents, it will behave as a DNAPL once released to the environment (USEPA, 1994).

The bulk of the DNAPL will continue to behave as a separate, relatively insoluble fluid-phase migrating very slowly downward through the soil while the individual components partition into various phases. The partitioning behavior will be due to different affinities for soil and water, represented by the Kow and water solubility parameters, respectively.

These two parameters are included in Table 1 and are directly proportional to their respective affinities. A higher Kow indicates a higher affinity for soil, and a higher solubility indicates a higher affinity for water.

Because some of the constituents are more dense than water, they can continue to move downward under the influence of gravity past the ground water table and into the aquifer. Since the maximum stable ganglia (or "finger") length is greater below the

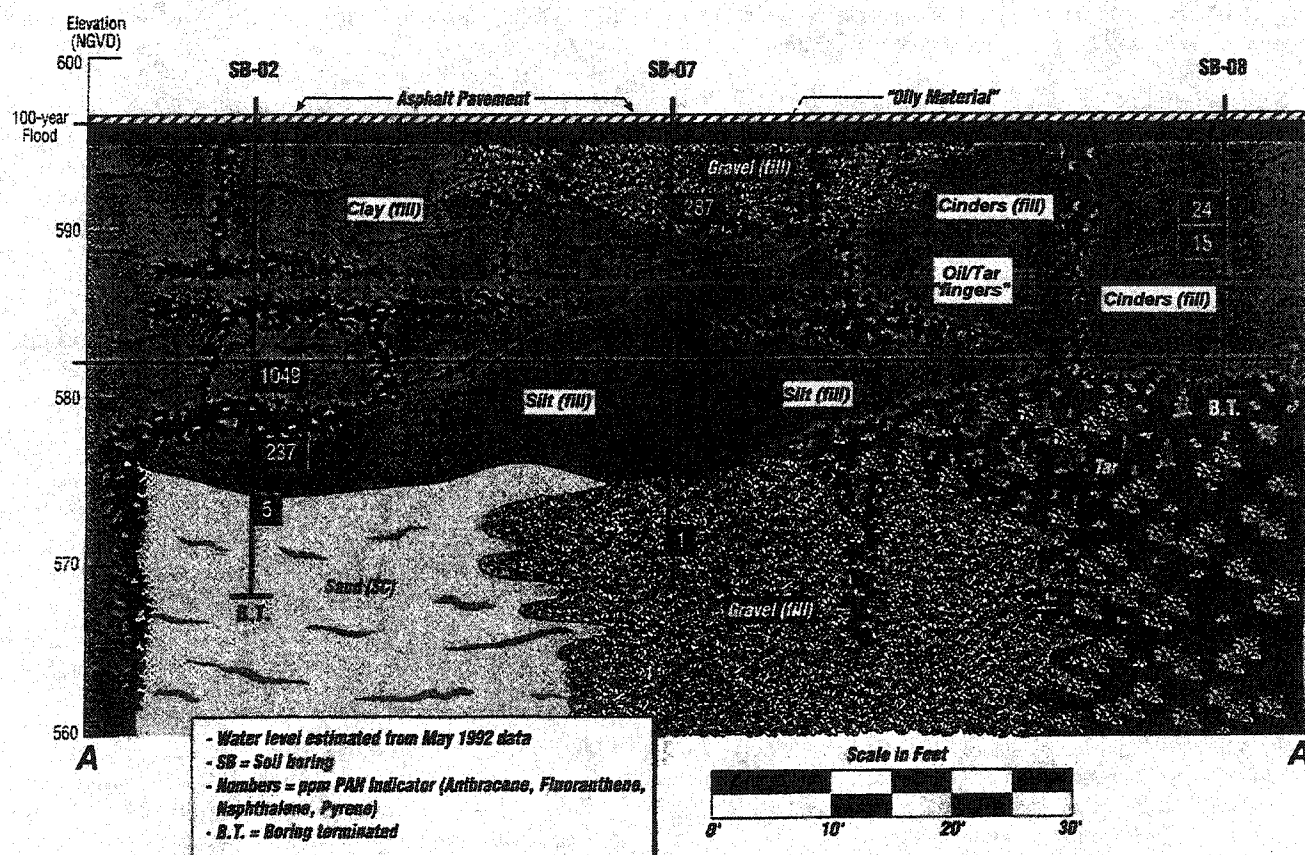


Figure 2. Cross-section A-A' through center of site near the former 6K and 12K-ft³ gas holder locations.

water table than in the vadose zone, the DNAPL can continue to migrate to greater depths (Sitar, et al, 1987). Migration will continue until encountering an "impermeable" layer such as the siltstone or limestone bedrock.

Using the analysis of Sitar, et al (1987), The maximum stable ganglia in the vadose zone was estimated at about 10 meters (33 feet), and 280 meters below the water table. Ganglia shorter than these are trapped in the soil pores and will not be dislodged by gravity forces. As a result, significant quantities of coal tar and other by-products can remain immobilized in the vadose zone and aquifer.

While the whole material may be slowly moving or immobile as a separate DNAPL phase, some portion of the individual component species may leach into the ground water. Although there are many PAHs in gas plant by-products, most are high molecular weight compounds with very limited solubility in water and a strong tendency to adsorb onto soils (as evidenced by the relatively high Kow values in Table 1). Therefore, most PAHs do not tend to migrate far beyond the primary source material area.

The exceptions include naphthalene (molecular weight 128, water solubility 32 mg/l, Kow 2760) and other light PAHs such as acenaphthylene, acenaphthene, fluoranthene, phenanthrene, and pyrene (all with molecular weights less than 200 and Kow less than 30,000). These lighter species are not as strongly adsorbed on soils and are, therefore, more likely to migrate with the ground water flow from the original source area.

The light aromatics sometimes found in gas plant by-products include benzene, toluene, and xylene. These compounds are moderately soluble (175-1750 mg/l) and are only slightly adsorptive on soil organic matter.

Records available at GEPD indicate the extent of migration has not been well defined. Detection limits for organic contaminants in groundwater were not calculated to the practical quantitation limit (PQL). State standards require organic contamination in groundwater to be defined to background levels defined by the PQL.

Toxicity of Coal Tar Wastes and Threats to Human Health and the Environment

The properties surrounding the site are generally commercial with some limited residential uses. It is supplied with municipal potable water and no present or past uses of wells for drinking water are recorded. However, a water well survey of the vicinity demonstrated that the underlying aquifer is a proven resource and will be subject to stringent protection by the GEPD.

Most of the compounds leaching from MGP wastes are suspect or known carcinogens with relatively stringent regulatory standards for drinking water or dermal contact. In particular, benzene in groundwater and benzo(a)pyrene (BaP) in soils are among the most serious concerns.

Given the residential use of the site, and a proven groundwater resource, the likely standard applied to the site would be 0.005 mg/l benzene in groundwater and 2.0 mg/kg BaP in soils. Table 1 indicates concentrations in the site media significantly exceed these standards.

Other less stringent standards may be established by a more detailed toxicological and/or contaminant fate and transport modeling process. Alternatively, the site may be converted to non-residential use with restrictive covenants attached to the property title prohibiting groundwater use, etc.

2.3 Estimated Volume of DNAPL Release.

Based upon the data in Table 1, an estimate of the total NAPL partitioning was calculated for the contaminated area of the site. Using a mass-balance approach, the calculation included terms incorporating fugacity to evaluate multi-phase partitioning.

The best groundwater data were from samples collected and analyzed from well MW-07 located about 60 feet south of the former 6K gas holder and screened in the sand aquifer directly underneath highly-contaminated sandy, silty, clay fill and alluvium. Analytical results for the groundwater samples formed the baseline for evaluation of multi-phase partitioning. The unit total mass of contaminants was estimated from soil samples collected from borings SB-02 and SB-2II near the former 6K and 12K holders.

Well MW-07 appeared to have the most direct hydraulic connection with these soils. During higher river stages, the groundwater can reverse its normal gradient and flow to the south.

The data indicate the aforementioned soils and groundwater at well MW-07 were in equilibrium with benzene, xylenes, naphthalene, and phenanthrene. Equilibrium conditions were not as apparent with the other less mobile species.

Based upon the foregoing analyses, the total DNAPL partitioning was estimated at an average of 0.15 ft³/ft³ or m³/m³. Considering the results shown for naphthalene in Table 1, this should be a conservative estimate.

If it is assumed the ganglia web has affected a roughly conical volume with a maximum depth of 24 feet underneath the outlined area on Figure 1, then the volume of DNAPL can be calculated at approximately 300,000 gallons. This result is reasonable when we consider the plant was disposing of perhaps 22,000 gallons per year of by-product for several decades.

FINDINGS AND CONCLUSIONS

The subject site has been significantly contaminated by manufactured gas plant by-product wastes released over a period of several decades. Up to about 300,000 gallons of DNAPL may be bound up in the pore spaces of the most seriously affected soils. The contaminant constituents in the DNAPL have been formally designated a hazardous waste and are a serious concern to regulatory officials.

According to GEPD records, the site is used for residential purposes and is located in a downtown urban area on the banks of a major state river. Leaching and migration of contaminants from the affected soils by groundwater under the hydraulic influence of the river has resulted in spreading of contamination around most of the site. At a minimum, state regulations will require removal of all NAPL to the extent feasible using best available technology.

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